

Claims

1. A process for coating a metallic surface with an aqueous composition, also comprising, if desired, organic solvent and other components, which is substantially or entirely free from chromium(VI) compounds, for the purpose of pretreatment prior to a further coating or for treatment, which process is characterized in that the composition comprises, besides water,
- a) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-free silane and
- b) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-containing silane,
- the silanes in the composition being water-soluble or becoming water-soluble in particular by virtue of (further) hydrolysis reactions and/or chemical reactions prior to application to the metallic surface,
- the clean, pickled, cleaned and/or pretreated metallic surface being contacted with the aqueous composition and a film being formed on the metallic surface and subsequently dried and, if desired, additionally cured,
- the dried and, where appropriate, also cured film having a thickness in the range from 0.001 to 10 μm .
2. Process according to claim 1, characterized in that in the aqueous composition selected from the fluorine-free silanes there is in each case at least one acyloxysilane, alkoxysilane, silane having at least one amino group such as an

aminoalkylsilane, silane having at least one succinic acid group and/or succinic anhydride group, bis-silyl-silane, silane having at least one epoxy group such as a glycidyloxysilane, (meth)acrylato-silane, multi-silyl-silane, ureido-silane, vinylsilane and/or at least one silanol and/or at least one siloxane or siloxane whose composition corresponds chemically to that of the aforementioned silanes.

3. Process according to claim 1 or 2, characterized in that there is at least one fluorine-free silane selected from the group consisting of, or based on,

glycidyloxyalkyltrialkoxysilane,
methacryloyloxyalkyltrialkoxysilane,
(trialkoxysilyl)alkylsuccinoysilane,
aminoalkylaminoalkylalkyldialkoxysilane,
(epoxycycloalkyl)alkyltrialkoxysilane,
bis(trialkoxysilylalkyl)amine,
bis(trialkoxysilyl)ethane,
(epoxyalkyl)trialkoxysilane,
aminoalkyltrialkoxysilane,
ureidoalkyltrialkoxysilane,
N-(trialkoxysilylalkyl)alkylenediamine,
N-(aminoalkyl)aminoalkyltrialkoxysilane
N-(trialkoxysilylalkyl)dialkylenetriamine,
poly(aminoalkyl)alkyldialkoxysilane,
tris(trialkoxysilyl)alkyl isocyanurate,
ureidoalkyltrialkoxysilane and
acetoxysilane.

4. Process according to one of the above claims, characterized in that there is at least one silane selected from the group consisting of, or based on,

3-glycidyloxypropyltriethoxysilane,

3-glycidyloxypropyltrimethoxysilane,
3-methacryloyloxypropyltriethoxysilane,
3-methacryloyloxypropyltrimethoxysilane,
3-(triethoxysilyl)propylsuccinoysilane,
aminoethylaminopropylmethyldiethoxysilane,
aminoethylaminopropylmethyldimethoxysilane,
beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane,
beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
beta-(3,4-epoxycyclohexyl)methyltriethoxysilane,
beta-(3,4-epoxycyclohexyl)methyltrimethoxysilane,
gamma-(3,4-epoxycyclohexyl)propyltriethoxysilane,
gamma-(3,4-epoxycyclohexyl)propyltrimethoxysilane,
bis(triethoxysilylpropyl)amine,
bis(trimethoxysilylpropyl)amine,
(3,4-epoxybutyl)triethoxysilane,
(3,4-epoxybutyl)trimethoxysilane,
gamma-aminopropyltriethoxysilane,
gamma-aminopropyltrimethoxysilane,
gamma-ureidopropyltrialkoxysilane,
N-(3-(trimethoxysilyl)propyl)ethylenediamine,
N-beta-(aminoethyl)-gamma-aminopropyltriethoxysilane,
N-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane,
N-(gamma-triethoxysilylpropyl)diethylenetriamine,
N-(gamma-trimethoxysilylpropyl)diethylenetriamine,
N-(gamma-triethoxysilylpropyl)dimethylenetriamine,
N-(gamma-trimethoxysilylpropyl)dimethylenetriamine,
poly(aminoalkyl)ethyldialkoxysilane,
poly(aminoalkyl)methyldialkoxysilane,
tris(3-(triethoxysilyl)propyl) isocyanurate,
tris(3-(trimethoxysilyl)propyl) isocyanurate and
vinyltriacetoxysilane.

5. Process according to one of the above claims,
characterized in that in the aqueous composition
selected from the fluorine-containing silanes
there is in each case at least one acyloxysilane,
alkoxysilane, silane having at least one amino
group such as an aminoalkylsilane, silane having

at least one succinic acid group and/or succinic anhydride group, bis-silyl-silane, silane having at least one epoxy group such as a glycidyloxysilane, (meth)acrylato-silane, multi-silyl-silane, ureidosilane, vinylsilane and/or at least one silanol and/or at least one siloxane or polysiloxane whose composition corresponds chemically to that of the aforementioned silanes, containing in each case at least one group that contains at least one fluorine atom.

6. Process according to one of claims 1 or 5, characterized in that the aqueous composition comprises at least one fluoroalkoxyalkylsilane, at least one mono-, di- or trifunctional fluorosilane, at least one mono-, bis- or tris-fluorosilane, at least one fluorosilane based on ethoxysilane and/or based on methoxysilane and/or at least one fluorosilane having at least one functional group such as, for example, an amino group, in particular in the form of a cocondensate, such as, for example, a fluoroalkyldialkoxysilane, a fluoroaminoalkylpropyltrialkoxysilane, a fluoromethanesulfonate, a fluoropropylalkyldialkoxysilane, a triphenylfluorosilane, a trialkoxyfluorosilane, a trialkylfluorosilane and/or a tridecafluorooctyltrialkoxysilane.

7. Process according to one of claims 1, 5 or 6, characterized in that the silane contains at least two amino groups and also at least one ethyl group and/or at least one methyl group.

8. Process according to one of the above claims, characterized in that the aqueous composition also comprises at least one metal chelate and/or at least one oligomer/polymer/copolymer (components c) and d) respectively).

9. Process according to one of the above claims, characterized in that in the aqueous composition there is also at least one component e) selected from the group consisting of
- 5 e₁) at least one inorganic compound in particle form, having an average particle diameter, measured on a scanning electron microscope, in the range from 0.005 to 0.3 μm in diameter,
- 10 e₂) at least one lubricant,
- e₃) at least one organic corrosion inhibitor,
- e₄) at least one anti-corrosion pigment,
- e₅) at least one agent for neutralizing and/or sterically stabilizing the synthetic resins,
- 15 e₆) at least one organic solvent,
- e₇) at least one siloxane,
- e₈) at least one long-chain alcohol, and
- e₉) at least one surfactant.
- 20 10. Process according to one of the above claims, characterized in that the organic film former is a synthetic resin mixture of at least one polymer and/or at least one copolymer, comprising synthetic resin based on acrylate, epoxide,
- 25 ethylene, urea-formaldehyde, phenol, polyester, polyurethane, styrene, styrene-butadiene and/or vinyl.
11. Process according to one of the above claims, characterized in that the organic film former also comprises as synthetic resin a content of organic polymer, copolymer and/or mixtures thereof based on polyethyleneimine, polyvinyl alcohol, polyvinylphenol, polyvinylpyrrolidone and/or poly-
- 30 aspartic acid, in particular copolymers with a phosphorus-containing vinyl compound.
12. Process according to one of the above claims, characterized in that the acid groups of the
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synthetic resins are stabilized with ammonia, with amines such as morpholine, dimethylethanolamine, diethylethanolamine or triethanolamine and/or with alkali metal compounds such as sodium hydroxide.

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13. Process according to one of the above claims, characterized in that the aqueous composition contains from 0.1 to 980 g/l of the organic film former, preferably from 2 to 600 g/l.

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14. Process according to one of the above claims, characterized in that the amount of at least one fluorine-free silane in the aqueous composition, including the reaction products formed therefrom, is preferably from 0.05 to 300 g/l.

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15. Process according to one of the above claims, characterized in that the amount of at least one fluorine-containing silane in the aqueous composition, including the reaction products formed therefrom, is preferably from 0.01 to 150 g/l.

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16. Process according to one of the above claims, characterized in that the at least one metal chelate is selected from chelate complexes based on acetylacetonates, acetoacetic esters, acetonates, alkylenediamines, amines, lactates, carboxylic acids, citrates and/or glycols, the amount of at least one chelate in the aqueous composition, including any reaction products formed therefrom, being preferably from 0.1 to 80 g/l.

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17. Process according to one of the above claims, characterized in that as inorganic compound in particle form a finely divided powder, a dispersion or a suspension such as a carbonate,

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oxide, silicate or sulfate is added, especially colloidal and/or amorphous particles.

18. Process according to one of the above claims,
5 characterized in that as inorganic compound in particle form particles are added based on at least one compound of aluminum, of barium, of cerium, of calcium, of lanthanum, of silicon, of titanium, of yttrium, of zinc and/or of zirconium.
- 10 19. Process according to one of the above claims, characterized in that as lubricant at least one wax is used selected from the group consisting of paraffins, polyethylenes and polypropylenes, in
15 particular an oxidized wax, the amount of waxes in the aqueous composition being preferably in the range from 0.01 to 5% by weight.
- 20 20. Process according to one of the above claims, characterized in that the coating is partly produced by drying and filming and/or is cured by actinic radiation, cationic polymerization and/or thermal crosslinking.
- 25 21. Process according to one of the above claims, characterized in that the aqueous composition comprises at least one additive, in particular at least one selected from the group consisting of at least one biocide, at least one defoamer and/or at
30 least one wetting agent.
22. Process according to one of the above claims, characterized in that the coated metallic surface is dried at a temperature in the range from 20 to
35 400°C forced-air temperature.
23. Process according to one of the above claims, characterized in that the aqueous composition is

applied by rolling, flow coating, knife coating, spraying, squirting, brushing or dipping and if desired by subsequent squeezing off with a roller.

5 24. Process according to one of the above claims, characterized in that in each case at least one coating of printing ink, film, paint, paint-like material, powder coating material, adhesive and/or adhesive backing is applied to the dried and also,
10 where appropriate, cured film.

25. Process according to one of the above claims, characterized in that the coated metal parts, strips or strip sections are formed, painted,
15 coated with polymers such as PVC, for example, printed, bonded, hot-soldered, welded and/or joined with one another or with other elements by clinching or other joining techniques.

20 26. An aqueous composition for pretreating a metallic surface prior to a further coating or for treating the said surface, characterized in that the composition comprises, besides water,

25 a) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-free silane and

b) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-containing silane,
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the proportion of a) to b) in each case including the reaction products formed therefrom being preferably in the range from 1:0.01 to 1:4 and

35 the silanes in the composition being water-soluble or in particular water-soluble owing to (further) hydrolysis reactions and/or chemical reactions.

27. The use of the substrates coated by the process according to at least one of claims 1 to 26 above as wire, strip, sheet or part for a wire winding, a wire mesh, a steel strip, a metal sheet, a panel, a shield, a vehicle body or part of a vehicle body, a part of a vehicle, trailer, mobile home or missile, a cover, a casing, a lamp, a light, a traffic light element, a furniture item or furniture element, an element of a household appliance, a frame, a profile, a molding of complex geometry, a guideboard element, radiator element or fencing element, a bumper, a part of or with at least one pipe and/or profile, a window frame, door frame or cycle frame or a small part such as a bolt, nut, flange, spring or a spectacle frame.
28. The use of the composition according to at least one of claims 1 to 26 as an after-rinse solution, which is applied to a previous coating such as, for example, to a conversion coating, and/or as a composition for bright corrosion protection.